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**The following information is taken from the documents submitted by the applicant.**

**(54) Control of the Crystallization of Polyesters through Their Water Content**

**(57)** The invention relates to a process for the crystallization of an at least partially amorphous, thermoplastic polymeric material, which was obtained from a polymer melt by solidification, characterized by the fact that, prior to the step of the crystallization, the polymeric material is subjected to one or more conditioning steps, in which a controlled moisture content and/or a controlled moisture profile is adjusted in the material, or that the solidification from the polymer melt takes place in such a way that, prior to the step of the crystallization, the polymeric material has a defined initial moisture profile.

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## Description

**[0001]** The invention relates to a process for the crystallization of an at least partially amorphous, thermoplastic polymeric material, which was obtained from a polymer melt by solidification, in accordance with the preamble of claim 1 or claim 16.

**[0002]** Polyesters, such as polyethylene terephthalate, polyethylene naphthalate, etc., are obtained by synthesis in the melt. The solid polyester or copolyester material obtained from the melt by solidification is processed predominantly in amorphous form in subsequent processes, such as injection molding, extrusion, or thermoforming to fibers or articles, such as bottle parisons, its material properties, such as moisture, molecular weight, or crystallinity, being often intentionally or unintentionally and purely fortuitously modified in intervening processes, such as, for example, granulation, storage, crystallization, drying, or solid-state polycondensation.

**[0003]** In order to carry out better the intervening processes, polyester materials obtained from the melt synthesis or recycled by melting are solidified in granulate form or else strand form and ribbon form. The transformation to the solid form can hereby occur after the solidification of the polymeric material, as in the case of strand granulation, or from the still fluid state with subsequent solidification, as in the case of tablet formation or in a prilling tower. The solidification can take place under water or in a gaseous medium, such as steam, air, or nitrogen.

**[0004]** The storage of the granulate usually takes place in a silo or in sacks under uncontrolled conditions, for which the residence time, the temperature, or the relative humidity are fortuitous. During this time, the hygroscopic polyester material can take up moisture in an uncontrolled manner or even dry out, depending on the surroundings.

**[0005]** The drying and the solid-state polycondensation usually take place continuously in one tower or batchwise in a drum drier. The volatile molecules, such as, for example, water and ethylene glycol, are withdrawn from the product through a vacuum in a drum drier and through a stream of hot gas in a tower. The drying prevents a loss of molecular weight due to hydrolysis when the material is remelted in an extruder. The solid-state polycondensation leads to better product properties due to an increase in molecular weight. The drying and the solid-state polycondensation usually occur above

the temperature at which the material begins to crystallize, this resulting in a crystallization step.

[0006] The crystallization takes place at a temperature above the glass transition point, it being necessary to keep the granulate in motion in order to prevent the material from sticking together or clumping. This is achieved through a medium, such as air, nitrogen, water, or steam, in a fluidized bed, through a mechanical stirrer apparatus, or, in a drum drier, through rotation. Accordingly, in these crystallization processes, the time course of the exposure temperature and the exposure time or residence time of the pellet in the crystallizer is adjusted. The crystallization increases the stickiness point of the material and prevents a clumping or an agglomeration of the material in a subsequent drying or solid-state polycondensation.

[0007] However, it has been shown that, during such a crystallization, in spite of careful temperature control, an agglomerate formation by a number of pellets and/or a deformation of pellets up to a bursting of the pellet can nonetheless take place in the crystallizer. Such agglomerate formations and deformations during the crystallization seem to be favored by improper conditions during the granulate formation and/or by an improper storage of the granulate prior to the crystallization.

[0008] The present invention is based on the object of preventing such agglomerations and deformations of pellets, obtained from crystallizable, thermoplastic material, during a crystallization or during crystallization of the pellet.

[0009] This object is solved in accordance with claim 1 or 16 in that, prior to the step of the crystallization, the polymeric material is subjected to one or more conditioning steps, in which a controlled moisture content and/or a controlled moisture profile is adjusted in the material, or by the fact that the solidification from the polymer melt takes place in such a way that, prior to the step of the crystallization, the polymeric material has a defined initial moisture profile.

[0010] It is generally known that water causes a nucleating effect in polyesters and polymers, in general, which can have an influence on their crystallization behavior. Namely, it has been found that, through the adjustment of the moisture content and/or the moisture profile of the material, it is possible to influence substantially its subsequent crystallization and thus properties such as the tendency toward sticking together or

deforming. Even the reaction rate of a possibly further solid-state polycondensation can be thereby influenced. Thus, for example, in those regions of the polymeric material with a higher moisture, many small crystals form relatively rapidly, albeit with a smaller condensation rate in a subsequent solid-state polycondensation, whereas those regions of the polymeric material with lower moisture form less large crystals relatively slowly, but a larger condensation rate in a subsequent solid-state polycondensation can be expected.

**[0011]** The polymeric material can involve a polycondensate like polyester or polyamide, such as, for example, polyethylene terephthalate, polyethylene naphthalate, polybutylene naphthalate, or the copolymers thereof, it being possible to obtain these from new material and/or from recycled material.

**[0012]** In an appropriate manner, each conditioning step occurs in a medium with a certain water content at a certain temperature over a certain period of time. This makes possible a controlled diffusion into the polymeric material (wetting) or out of it (drying). Thus obtained at the end of the conditioning is a defined moisture distribution in the polymeric material. Preferably, the polymeric material is introduced directly after the solidification into a medium for the conditioning.

**[0013]** The polymeric material can have a non-defined moisture content and/or a non-defined moisture profile prior to the conditioning.

**[0014]** In an appropriate manner, at least one step for the conditioning of the material is a step for wetting the polymeric material or a step for drying the polymeric material, the conditioning having, in particular, a step for predrying. In this way, it is possible in the case of starting material with unknown moisture content and/or unknown moisture distribution, for example, to create largely known starting conditions for the further conditioning.

**[0015]** In an advantageous embodiment of the process of the invention, the step of predrying occurs over 0.5 min to 4 h, preferably 2 min to 30 min, under water or in steam under constant conditions in regard to temperature and pressure or over 15 min to 72 h, preferably 4 h to 24 h, in moist gas under constant conditions in regard to temperature and moisture quantity.

**[0016]** In a further advantageous embodiment of the process of the invention, the step of predrying occurs over 1 min to 72 h, preferably over 30 min to 24 h, in a dry

stream of gas under constant conditions in regard to temperature and residual moisture quantity or under vacuum under constant conditions in regard to temperature and pressure.

**[0017]** In an appropriate manner, one step for the conditioning can also take place at a temperature below the crystallization temperature of the polymeric material.

**[0018]** The polymeric material can also be obtained from the polymer melt by solidification in such a way that the polymeric material has a defined initial moisture profile prior to the step of the crystallization. This saves a preceding drying or a preceding wetting prior to the actual conditioning.

**[0019]** In particular, the defined initial moisture profile of the polymeric material can assume such a course that the surface of the polymeric material has a lower water content and the center has a higher water content. It is also possible that the defined initial moisture profile of the polymeric material assumes such a course that the polymeric material has a constant moisture profile from the surface to the center. The defined initial moisture profile of the polymeric material can also assume such a course that the surface of the polymeric material has a higher water content and the center has a lower water content. The lower water content in the center can, for example, be locally constant, the surface with the higher water content preferably extending into the polymeric material over at most 20% of the stretch from the surface to the center. All of these adjustments of the moisture profile occur relatively rapidly for sufficiently high conditioning temperatures. Accordingly, the inhomogeneous moisture distributions thus obtained can largely compensate for undesired diffusion processes, particularly of water molecules, in the polymeric material during its storage. It could also be stated that the storage of the polymeric material under certain conditions (temperature, water content of the air, period of storage) is regarded as a part of the conditioning, so that, after the conditioning under defined conditions, the desired moisture distribution is present in the material.

**[0020]** Preferably, the subsequent crystallization of the polymeric material occurs in a hot stream of gas.

**[0021]** In an appropriate manner, the steps for conditioning occur continuously, particularly a step for drying, solid-state polycondensation, or solid-state polyaddition occurring after the step of the crystallization.

**[0022]** Further advantages, features, and possible applications of the invention ensue from the following description.

**[0023]** The process of the invention is, for example, a process for treating crystallizable polymer materials, as new material or as recycled material, particularly polyester materials such as PET or RPET, by the following steps: feeding of the polymer material into a first reaction chamber, it being present in the first reaction chamber at least temporarily as a melt; forming and cooling of the melted polymer material to units consisting of solidified polymer material; conveying of the solidified polymer material into a second reaction chamber for adjustment of the moisture content and/or the moisture distribution of the units consisting of solidified polymer material; and feeding of the polymer material into a third reaction chamber for crystallization of the solidified polymer material of the units. Prior to the adjustment of the moisture content of the units consisting of solidified polymer material in the second reaction chamber, the water is withdrawn from, for example, the melted polymer material in the first reaction chamber, apart from a certain residual water content, by exposing the formed and solidified units consisting of polymer material to a medium with a certain moisture content and a certain temperature for a certain period of time in the second reaction chamber, for example, for adjustment of the moisture content and/or the moisture distribution of the units consisting of solidified material. The withdrawal of water out of the melted polymer material in the first reaction chamber occurs, for example, through vacuum melt degassing. The medium with the certain moisture content and the certain temperature is, for example, a hot water bath, which, for example, is placed under pressure and maintained at temperature of more than 100°C, or the medium is an atmosphere containing superheated steam. Coming into consideration as the first reaction chamber is, for example, the process chamber of a polycondensation reactor or extruder, particularly a ring extruder. The melted polymer material at the extruder end is formed, for example, into one or several strands, which are then cooled and solidified.

**[0024]** The cooling and solidifying of the strands when they enter the second reaction chamber occurs, for example, by means of the medium mentioned above. The one or the several strands are conveyed, for example, continuously through the second reaction chamber, the strands being guided, in particular, in such a way that they do not touch one another. After they pass through the second reaction chamber, for example, the strands are chopped into pellets or, after they have passed through the second reaction chamber, they are granulated or pulverized. For adjustment of the moisture content of the strands, the strand diameter, the temperature of the medium, and the time during which the strands are exposed to the medium, for example, are chosen in such a way that a homogeneous moisture distribution is afforded over the entire strand volume. At the extruder end, the melted polymer material can also be formed into one or several strands and chopped into pellets, which are then cooled and solidified, the cooling and solidifying of the pellets occurring here, too, by means of the medium, upon entering the second reaction chamber. The pellets are conveyed hereby continuously through the second reaction chamber and this is preferably done in such a way they touch one another not at all or only briefly. The medium is hereby kept in constant motion and mixed together. The pellets can be swirled during the motion of the medium. For the adjustment of the moisture content of the pellets, similarly to the strands, the size of the pellets, the temperature of the medium, the moisture content of the medium, and the time during which the pellets are exposed to the medium can be chosen in such a way that a homogeneous moisture distribution is afforded over the entire pellet volume or that an inhomogeneous moisture distribution is afforded in the pellet volume. The time during which the pellets are exposed to the medium can also be chosen to be shorter than the time of exposure required to attain a uniform moisture distribution in the pellets. The temperature of the medium and/or the moisture content of the medium are changed in, for example, the course of the exposure to the medium in the second reaction chamber in such a way that a more or less strongly wetting character of the medium or a more or less strong dewetting character of the medium is afforded. In particular, the parameters of temperature and water content of the medium are changed in the course of the exposure in such a way that the medium is wetting at the beginning of the exposure and dewetting at the end of the exposure or that the medium is dewetting at the beginning of the

exposure and wetting at the end of the exposure. The treatment step in the second reaction chamber can occur either batchwise, the change in the parameters of the medium in the course of the exposure occurring with time, or it can occur continuously, the change in the parameters of the medium in the course of the exposure occurring locally along the path of the pellet through the second reaction chamber. The third reaction chamber is, for example, the process chamber of a crystallizer, particularly a multistage crystallizer. Following the step of the crystallizer in the third reaction chamber, a further step for drying or solid-state polycondensation in a fourth reaction chamber can ensue, this involving, for example, the process chamber of a solid-state polycondensation reactor, particularly a tower reactor.

#### Embodiment Example 1

**[0025]** Recycled PET material (RPET) is fed into an extruder, which represents a first reaction chamber. The RPET material is melted in the extruder and the melted polymer material is formed at the extruder end into several strands, which are then cooled and solidified. The cooling and the solidifying of the strands occurs in a second reaction chamber, which is formed by a hot water bath that stands under pressure and has a temperature of more than 100°C. The several strands consisting of solidified polymer material are conveyed continuously through the hot water bath, the strands being guided in such a way that they do not touch one another. After they have passed through the water bath in the second reaction chamber, the strands are chopped into pellets. For adjustment of the moisture content of the strands, the strand diameter, the temperature of the water bath, and the time during which the strands are exposed to the water bath are chosen in such a way that a homogeneous moisture distribution is afforded over the entire strand volume. Subsequently, the pellets obtained from the strands are fed into a multistage crystallizer, which constitutes the third reaction chamber. Occurring as further treatment step is a solid-state polycondensation in a tower reactor, which constitutes a fourth reaction chamber.



## Embodiment Example 2

**[0026]** Recycled polyethylene terephthalate (RPET) is fed into an extruder, which constitutes the first reaction chamber. The melted polymer material is formed at the extruder end into strands and immediately chopped into pellets. The chopped pellets enter a second reaction chamber, which is formed by a hot water bath. The pellets are conveyed continuously through the hot water bath, it being ensured that they touch one another not at all or only briefly by keeping the water in constant motion and mixing it together, the pellets being swirled by the motion of the water. For the adjustment of the moisture content of the pellets, the pellet size, the temperature of the water bath, and the time during which the pellets are exposed to the water are chosen in such a way that a homogeneous moisture distribution is afforded over the entire pellet volume. Subsequently, the pellets treated in this manner enter a multistage crystallizer, which represents the third reaction chamber, after which they are subjected to a solid-state polycondensation in a tower reactor, which represents the fourth reaction chamber.

**[0027]** Both in the Embodiment Example 1 and in the Embodiment Example 2, the exposure of the strands or the pellets to the hot water bath makes it possible to achieve overall a more or less strongly wetting character or a more or less strongly dewetting character of the water bath on the polymer material.

## Embodiment Example 3

**[0028]** The procedure is the same as for Embodiment Example 1 and Embodiment Example 2, but, in place of the hot water bath, an atmosphere of superheated steam is used as medium in the second reaction chamber. The parameters of temperature and water content of the atmosphere containing superheated steam are changed over the course of the exposure in the second reaction chamber in such a way that the atmosphere containing superheated steam has a wetting effect at the beginning of the exposure and a dewetting effect at the end of the exposure.

## Patent Claims

1. Process for the crystallization of an at least partially amorphous, thermoplastic polymeric material, which was obtained from a polymer melt by solidification, **characterized by the fact that**, prior to the step of the crystallization, the polymeric material is subjected to one or more conditioning steps, in which a controlled moisture content and/or a controlled moisture profile is adjusted in the material.
2. Process in accordance with Claim 1, characterized by the fact that the polymeric material involves a polycondensate, such as polyester or polyamide.
3. Process in accordance with Claim 2, characterized by the fact that the polyester involves polyethylene terephthalate, polyethylene naphthalate, polybutylene naphthalate, or the copolymers thereof, it being possible to obtain these from new material and/or from recycled material.
4. Process in accordance with one of the preceding claims, characterized by the fact that each conditioning step occurs in a medium with a certain water content at a certain temperature over a certain period of time.
5. Process in accordance with one of the preceding claims, characterized by the fact that the polymeric material is introduced directly after the solidification into a medium for the conditioning.
6. Process in accordance with one of Claims 1 to 4, characterized by the fact that the polymer material has a non-defined moisture content and/or a non-defined moisture profile prior to the conditioning.
7. Process in accordance with one of the preceding claims, characterized by the fact that at least one step for the conditioning is a step for wetting of the polymeric material.
8. Process in accordance with Claim 7, characterized by the fact that the conditioning has a step for predrying.
9. Process in accordance with Claim 8, characterized by the fact that the step of predrying occurs over 0.5 min to 4 h, preferably 2 min to 30 min, under water or in steam under constant conditions in regard to temperature and pressure or over 15 min to 72 h, preferably 4 h to 24 h, in moist gas under constant conditions in regard to temperature and moisture quantity.

10. Process in accordance with Claim 6, characterized by the fact that at least one of the steps for conditioning is a step for drying of the polymeric material.
11. Process in accordance with Claim 10, characterized by the fact that the step of predrying occurs over 1 min to 72 h, preferably over 30 min to 24 h, in a dry stream of gas under constant conditions in regard to temperature and residual moisture quantity or under vacuum under constant conditions in regard to temperature and pressure.
12. Process in accordance with one of the preceding claims, characterized by the fact that one step for preconditioning takes place at a temperature below the crystallization temperature of the polymeric material.
13. Process in accordance with one of the preceding claims, characterized by the fact that the polymeric material is transformed into a granulate form, a strand form, or a ribbon form.
14. Process in accordance with Claim 13, characterized by the fact that the polymeric material is transformed into a granulate form after the solidification.
15. Process in accordance with Claim 13, characterized by the fact that the polymeric material is transformed from the still fluid state into a granulate form and subsequently is solidified.
16. Process for the crystallization of an at least partially amorphous, thermoplastic polymeric material, which was obtained from a polymer melt by solidification in such a way that, prior to the step of the crystallization, the material has a defined initial moisture profile.
17. Process in accordance with Claim 16, characterized by the fact that the defined initial moisture profile of the polymeric material assumes such a course that the surface of the polymeric material has a lower water content and the center has a higher water content.
18. Process in accordance with Claim 16, characterized by the fact that the defined initial moisture profile of the polymeric material assumes such a course that the polymeric material has a constant moisture profile from the surface to the center.
19. Process in accordance with Claim 16, characterized by the fact that the defined initial moisture profile of the polymeric material assumes such a course that the surface of the polymeric material has a higher water content and the center has a lower water content.
20. Process in accordance with Claim 19, characterized by the fact that the lower water content in the center is locally constant.

21. Process in accordance with Claim 20, characterized by the fact that the surface with the higher water content extends into the center into the polymer over at most 20% of the stretch from the surface.
22. Process in accordance with one of the preceding claims, characterized by the fact that the crystallization of the polymeric material occurs in a stream of hot gas.
23. Process in accordance with one of the preceding claims, characterized by the fact that the step for the conditioning occurs continuously.
24. Process in accordance with one of the preceding claims, characterized by the fact that, after the step of the crystallization, a step for solid-state polycondensation of solid-state polyaddition occurs.